ARES NO_x Sensor Development

Los Alamos National Laboratory

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Project Description, Goals, and Objectives

- Develop new, lost cost, high-temperature solid-state sensors to detect NO_x in the exhaust gas stream of a reciprocating engine.
  - Ceramic sensors that operate on electrochemical principles
- Sensors to control regenerative NO_x catalyst systems.
- Sensors must be inexpensive, robust, and be able to detect NO_x in regimes of PO_2, T, [NOx] characteristic of current recip engine technology
- Lifetime, stability, sensitivity, response time, sulfur tolerance, device reproducibility, cost, etc.

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Project Team - LANL

- LANL team has 10 years of experience in the development of gas sensor technology
  - Oxygen
  - Sulfur dioxide
  - Hydrocarbons
  - Carbon Monoxide

- LANL CRADA with USCAR to develop high temperature electrochemical sensors for OBD-II applications.

- FY 1997 - 2001

  - Sensors required to measure real-time NMHC concentrations post catalytic converter with minimum CO cross interference as possible replacement of dual O_2 sensor approach currently used.

  - Partners: Ford, GM, and Chrysler

- "Mixed Potential Hydrocarbon Sensor with Low Sensitivity to Methane and CO" submitted for U.S. Patent, Spring 2000.

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Project Team - con't

- Previous LANL sensor work examples:
  - LDRD sensor development work
    - "Controlled Interface Gas Sensors", U.S. Patent applied for 2002.
  - Sulfur resistant O_2 combustion control sensors
    - Winner 1999 R&D 100 award in collaboration with Rosemount Analytical Co.
    - U.S. Patent no. 6,277,256
  - Amperometric response, lean burn O_2 sensor work in collaboration with Delphi Automotive
    - U.S. Patent no.s 5,695,624 & 5,543,025

- University Collaboration : ARES NO_x sensor development work will be performed in collaboration with Dr. Eric Wachsman and his sensor team at the University of Florida

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Impact on Goals of ARES Program

- Advanced reciprocating engines require new sensor technologies to reduce emissions and improve over-all efficiency.
  - NO_x emissions monitoring and control
  - Engine control
  - Control of NO_x regeneration catalysts and systems

- E.g. NO_x emissions cannot exceed 50 - 150 ppm (0.1 g/hp-hr).

- A NO_x sensor is needed to monitor and control emissions systems.

- Currently there is no suitable sensing technology available that is low-cost sulfur tolerant, long-lifetime, etc.

Milestones completed and planned

- Assemble analytical NOx capability at LANL with resources that are available. Completed
- Fabricate devices for initial study to demonstrate proof-of-concept. Completed
- Test and calibrate analytical [NO_x] system and build new test stations.Underway
- Study factors that affect sensitivity, lifetime, response time.
- Study electrode materials - NO_x catalysis and electrocatalysis.
- Study electro-catalysis and NO_x mixed potential electrochemistry.
- Improve NO_x sensor.

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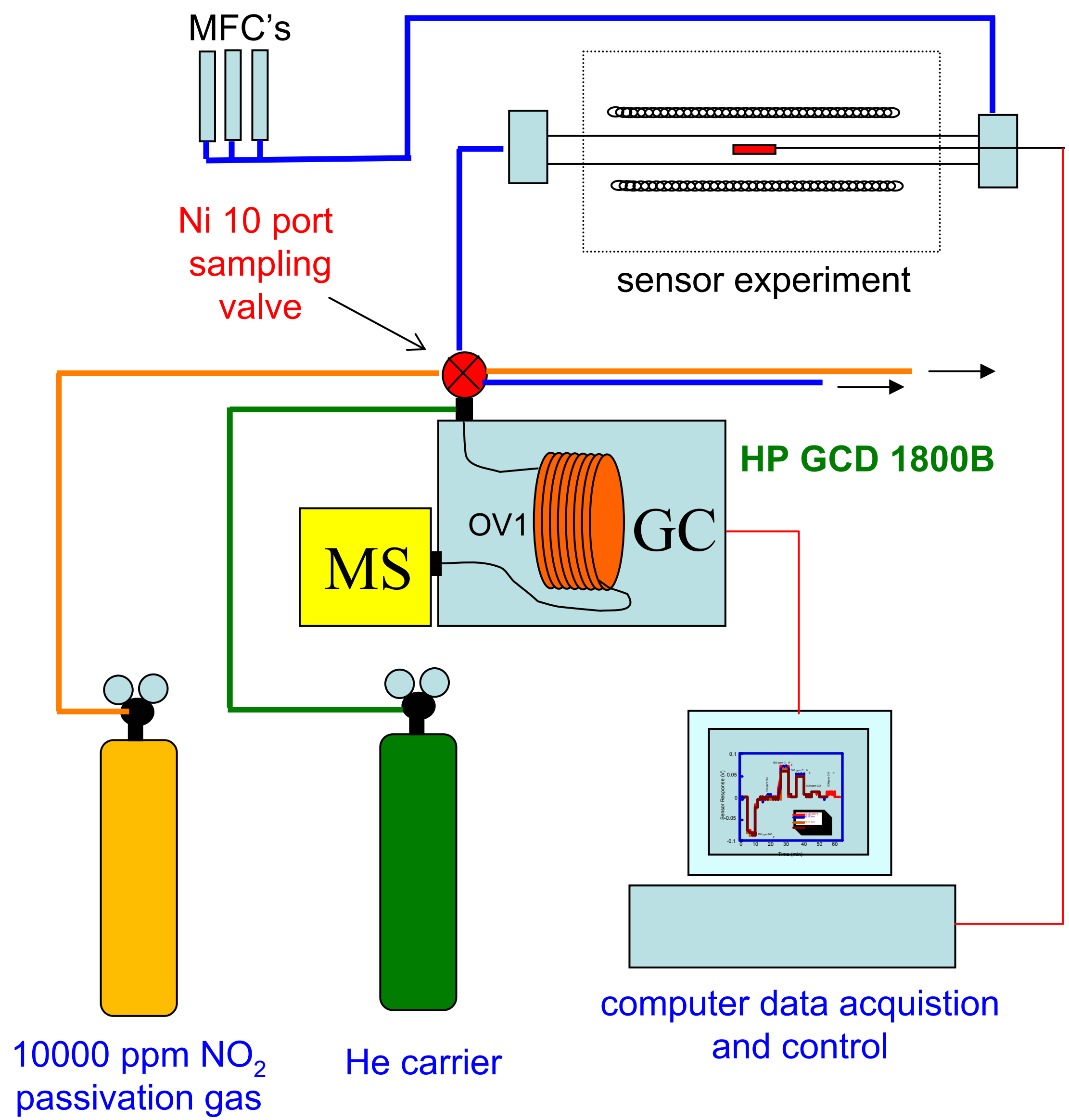
Development of NO_x Analysis Capability

- Program code received February 2002.
- First task was to build an in-house NO_x measurement capability.
  - $[NO_x]$ changes over time
  - Complex equilibrium in presence of O_2
- Capital equipment money to purchase commercial analytical NO_x analysis instrumentation was not approved.
- We have obtained and made modifications to a salvaged GC/MS system that may allow us to characterize $[NO_x]$ and study catalysis.



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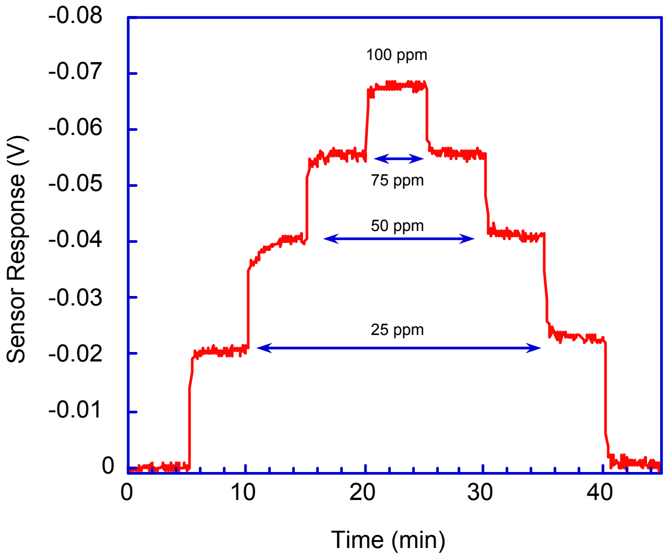
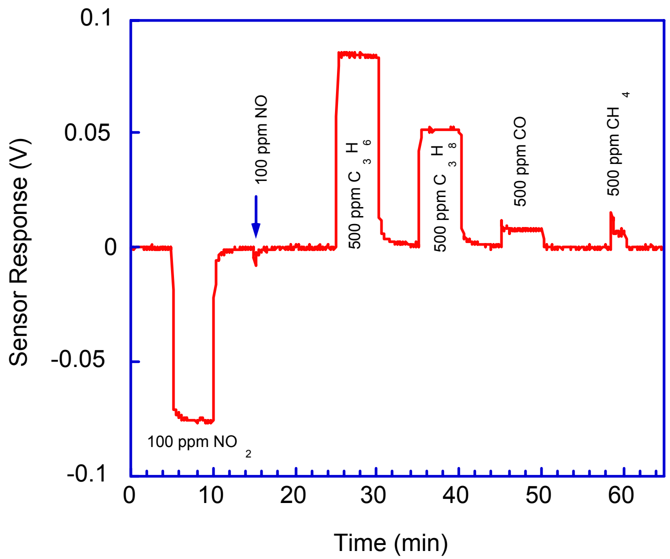
Preliminary Sensor Results

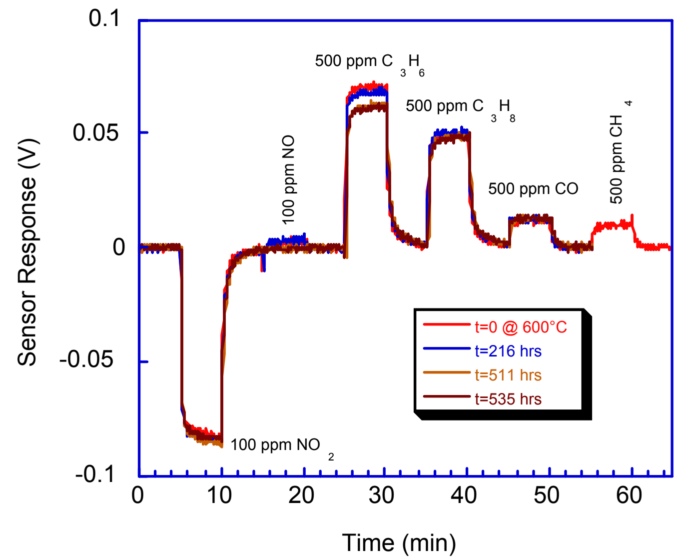
- Different metal oxide electrode selected based on observations of higher NO_x catalysis.
- Initial testing performed hot - 650°C and in 1%O_2
- Mixed potential response to NO_2 with no sensitivity to NO.
- Interference to CO and HC’s
  - almost 5:1 sensitivity to NO_2

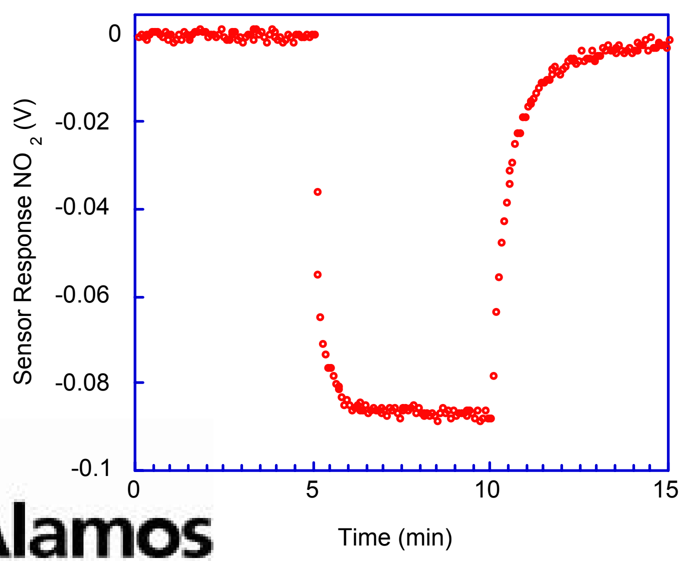


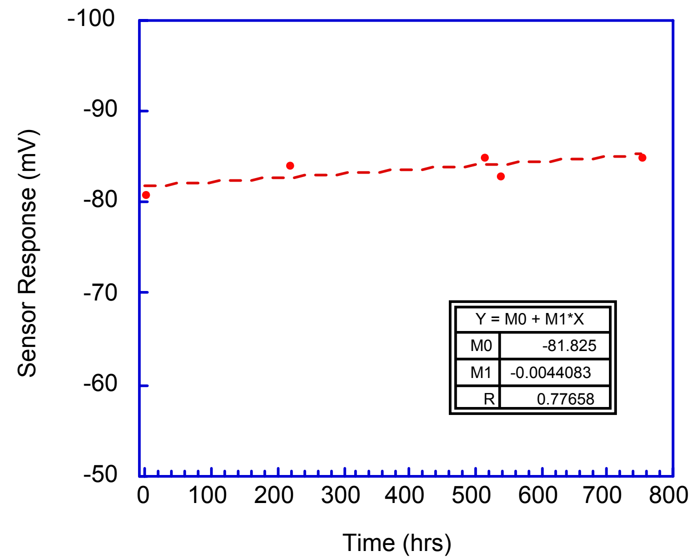


Preliminary Sensor Results - level stability and response time

- Two mixed potential sensors are currently being studied for:
  - Stability - 800 hrs
  - cross sensitivity - C_3H_6, C_3H_8, CO, CH_4
  - Reproducibility - two devices
  - response time has been measured but test system has not been optimized to permit quantification.
    - sensors are faster than the experimental set-up.
- Data below: 600°C, 1%O_2







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Key Technical Barriers and Project Risks

- Key technical barriers are:
  - Designing sensors with adequate sensitivity and selectivity
  - Elimination of cross interferences
  - Response stability over sensor lifetime
    - Electrode ageing phenomena

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Summary

- LANL NO_x sensor work commenced in February 2002.

- Assembly of gas chromatography mass spectroscopy system for analytical NO_x measurement complete. System is being tested and calibrated to see if method is viable to reliably measure concentrations of oxides of nitrogen.
- Fabricated several prototype mixed potential-based NO_x sensors for characterization.
- Demonstrated NO_2 response at 1%O_2 and in air at [NO_2] = 25-100 ppm
  - briefly examined level stability and potential for device fabrication with high device to device reproducibility - devices are excellent in both regards

- Expanding work to study factors which affect response time, NO_x sensitivity, cross sensitivity, temperature coefficients, device reproducibility, etc.

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